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IV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE PRODUCTS OF THE DRY DISTILLATION OF WOOD AT LOW TEMPERATURES.

By Charles F. Mabery.

Presented January 10th, 1883.

In the manufacture of acetic acid by the dry distillation of wood at low temperatures, as it is conducted by Dr. E. R. Squibb, of Brooklyn, N. Y., an oil heavier than water collects during the distillation in considerable quantities. Upon examination, Professor H. B. Hill* found that this oil contained a large percentage of furfurol, and that by the action of alkalies upon it a small quantity of pyroxanthin was formed. Further information concerning the more volatile products of the distillation therefore seemed desirable; and since different portions of the crude methyl alcohol were kindly placed at my disposal by Dr. Squibb, I undertook an examination of its constituents.

The composition of crude wood spirit has frequently been made the subject of investigation within a few years. Beside methyl alcohol and methyl acetate, which constitute the greater part of the product in the ordinary process of distillation, acetic aldehyde, acetic acid, aceton, acetal, dimethylacetal, methylethylketone, and allyl alcohol have been found in smaller quantities. Traces of the higher ketones have been detected in the less volatile portions, and in the high boiling oils small quantities of the aromatic hydrocarbons toluol, xylol, and cumol.

A study of the product under consideration shows that it has essentially the same composition. Its distinctive characteristic consists in different quantitative proportions of several constituents, probably due to the low temperature at which the first distillation was conducted.

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* These Proceedings, Vol. XVI. p. 192.

It also contains methyl formiate, which has not hitherto been recognized as a constituent of wood spirit.[*]

Three portions were selected for examination. The first portion (*a*) was collected at the beginning of the distillation, the second (*b*) after several hundred gallons had distilled, and the third (*c*) when the distillation of methyl alcohol was well advanced. Each portion was bright yellow in color, and from (*a*) and (*b*) a sharp penetrating odor was emitted. Since various attempts to remove the small percentage of water by desiccation were unsuccessful, the product was fractional as it was received. Anhydrous cupric sulphate absorbed only a small fraction of the water, even after standing several weeks, and fused potassic carbonate produced a decomposition, as shown by the color changing to a dark brown, with the formation of a yellow precipitate on standing. In the fractional distillation very satisfactory results were obtained, both in the separation of the different fractions and in economy of time, by the use of Hempel's[†] device for condensation.

The following table contains the results of the tenth fraction of each portion expressed in percentages. To insure a more complete condensation of the volatile products in (*a*), after passing through a Liebig's condenser, the distillate was cooled by a freezing mixture. Considerable gas escaped condensation at the beginning of the distillation, but it was found to consist chiefly of carbonic dioxide.

(*a*.)		(*b*.)		(*c*.)	
Temperatures.	Percentages.	Temperatures.	Percentages.	Temperatures.	Percentages.
20° - 25°	2.1				
25° - 30°	1.5				
30° - 40°	1.				
40° - 50°	1.				
50° - 52°	1.6				
52° - 54°	9.3	Below 54°	3.		
54° - 56°	62.8		74.1		
56° - 60°	7.3		3.6	Below 63°	4.7
Above 60°	6.7	60° - 70°	3.7	63° - 65°	2.5
		Above 70°	9.9	65° - 68°	57.9
				Above 68°	31.4
Loss	6.7		5.7		3.5

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[*] Krämer and Grodzky succeeded in isolating formic acid in small quantity from the oil obtained by adding sulphuric acid to the mother liquor of *Holzessig*, after removing the greater part of the acetic acid as sodic acetate. (Berichte deutsch. chem. Gesellsch., 1878, 1356.)

[†] Zeitschrift fur Anal. Chem., xx. 502.

The residue of the distillation in each case contained the greater part of the water, though in (*a*) it consisted chiefly of methyl alcohol. In (*b*) approximately one half of the residue consisted of the higher boiling oils, and in (*c*) it was composed beside water of furfurol and an oil of low specific gravity. The constituents of the various fractions will be described in detail.

Acetic Aldehyde.

In (*a*) the fraction that came over between 20° and 25° was very soluble in water, and it gave the penetrating odor characteristic of acetic aldehyde. This substance was also recognized in that portion of (*b*) which distilled below 54°, and in the fraction below 63° in (*c*). It formed a compound with acid sodic sulphite, crystallizing in flat prisms, which were very soluble in water. In order to establish its identity, an aqueous solution of the fraction 20° - 25° was boiled with an excess of silver oxide, filtered, and concentrated by evaporation. On cooling, silver acetate crystallized in characteristic forms, which, on analysis, gave the required percentage of silver.

I. 0.2222 grm. of the substance gave on ignition 0.1432 grm. Ag.
II. 0.3167 grm. of the substance gave on ignition 0.2050 grm. Ag.

	Calculated for $AgC_2H_3O_2$.	Found.	
		I.	II.
Ag	64.68	64.43	64.73

According to Krämer and Grodzky,* in the manufacture of wood spirit acetic aldehyde may usually be found in the first portions of the distillate. It is rarely present in large quantities, since, as they assert, the greater part is converted into dimethylacetal during the distillation.

Methyl Formiate.

This substance was isolated from the fractions 25° - 30° and 30° - 40°. On the addition of water an oil separated, which was purified by fractional distillation. There were thus obtained 8 grms. of a substance which distilled between 30° and 35°. It was saponified by boiling with an excess of plumbic hydrate, and the composition of the plumbic formiate determined by analysis.

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* Berichte deutsch. chem. Gesellsch., 1876, 1920.

I. 0.5214 grm. of the substance dried over H_2SO_4 gave on ignition with H_2SO_4 0.5296 grm. $PbSO_4$.

II. 0.2900 grm. of the substance gave 0.2960 grm. $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.	
		I.	II.
Pb	69.69	69.42	69.71

The presence of formic acid, and the quantity of the distillate which collected between 40° – 50°, suggested the possible formation of methylal. This fraction was therefore treated with an equal volume of water, and the oil which separated boiled with plumbic hydrate to decompose the methyl formiate. After drying with fused calcic chloride, the residue distilled above 50°. In another attempt to isolate methylal, 2,000 grms. of (*a*) were fractioned, and the distillate below 50° examined according to Dancer's method* for the separation of dimethylacetal. As in the first experiment, the residue distilled at a temperature far above the boiling point of methylal, which seemed to indicate that this substance could not have been formed in any appreciable quantity.

Methyl Acetate.

Since the fractions 50° – 52° and 52° – 54° gave reactions for aldehyde and acetone, they were evidently a mixture of these substances with methyl acetate. The greater part of the methyl acetate in (*a*) and (*b*) was collected in the fraction 54° – 56°, which boiled constant at 54°.5 – 55°.5 (Bar. 769.5 mm.). To determine approximately the percentage of methyl alcohol in this fraction, 655 grms. were saponified with potassic hydrate, and distilled. After drying with fused potassic carbonate and distilling off the methyl alcohol, there were obtained 255 grms., which came over between 66° and 67° (Bar. 769.5 mm.), or 92 per cent. of the amount required from the weight taken of methyl acetate. In repeating this saponification in a dilute solution of methyl acetate, with a potassic hydrate solution of known strength, the excess of alkali was titrated with standard sulphuric acid, and the percentage of methyl acetate calculated from the amount of potassic hydrate required to decompose it. This method gave 99.2 per cent of pure methyl acetate.

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* Ann. Chem. Pharm., cxxxii. 240.

Methyl Alcohol.

Although a small amount of methyl alcohol was contained in the higher fractions of (*a*) and (*b*), it was evidently condensed for the most part in the fraction 65° – 68° of (*c*). This fraction was slightly yellow in color, but no further attempts were made to determine its purity than an estimation of the percentage of acetone, which will presently be described.

Dimethylacetal.

The formation of dimethylacetal during the dry distillation of wood for the preparation of methyl alcohol was not observed until 1864, probably because of the small difference between its boiling point (64°) and that of methyl alcohol. After removing the methyl alcohol and acetone, Dancer* succeeded in separating a product which proved to be identical with dimethylacetal, made by heating methyl alcohol with acetic aldehyde. Krämer and Grodzky† state that it has since been recognized as a constant constituent of wood spirit. Its formation is probably due to the high temperature of the distillation, which enables the aldehyde to act upon the methyl alcohol. From the large percentage of aldehyde in the product under consideration, it would seem that this reaction had not taken place to any extent. Since an examination of the distillate below 65° in (*c*) failed to reveal the presence of dimethylacetal, a second portion of 2,000 grms. was fractioned, the lower fraction saponified and distilled over calcic oxide. The small amount of residue left after removing the methyl alcohol with calcic chloride, distilled at 57° – 58°, was readily miscible with water, and its reactions in general were characteristic of acetone. Dimethylacetal could not therefore have been formed in quantity sufficient for identification.

Acetone.

The first quantitative experiments on the influence of acetone upon the commercial value of methyl alcohol were made by Krämer and Grodzky.‡ They determined the quantity of dimethylaniline which could be obtained from a given weight of pure methyl alcohol, and also from methyl alcohol containing different amounts of acetone. Their results seemed to show that the yield was very considerably diminished if the quantity of acetone exceeded one per cent. Since crude wood spirit always contains a much higher percentage, it must be specially purified for the preparation of dimethylaniline.

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* Ann. Chem. Pharm., cxxxii. 240.

† Berichte deutsch. chem. Gesellsch., 1876, 1920.

‡ Ibid., 1880, 1005.

Various methods, dependent either upon the physical or the chemical properties of methyl alcohol, have been proposed for testing its purity. Krell[*] suggested a determination of the amount of methyl iodide which could be obtained by treating a given quantity of the alcohol with phosphorous iodide. In the hands of a skilful analyst the percentage of methyl alcohol may be accurately determined by this method; but, as Krämer remarked, it does not account for the nature of the impurities, and it is not sufficiently expeditious. To overcome these objections, Krämer[†] took advantage of the formation of iodoform from acetone. In his modification of Lieben's reaction,[‡] the formation of iodoform from ethyl alcohol and acetic acid is avoided, and acetic acid is only partially decomposed.

According to Krämer's method a mixture of 10 c.c. of a normal sodic hydrate solution, 5 c.c. of a double-normal iodine solution, and 1 c.c. of the alcohol to be tested, is shaken in a graduated cylinder with 10 c.c. of ether. 5 c.c. of the ether solution are withdrawn with a pipette, evaporated on a weighed watch-glass, and the residue weighed after drying in a warm desiccator. To obtain the weight of acetone in 1 c.c. of the alcohol, the weight of iodoform is multiplied by .28 if there are 9.5 c.c. of the ether solution.

The percentage of acetone in several fractions, as determined by this method, is given in the following table.[§] Since in each determination from 9 c.c. of the ether solution 5 c.c. were evaporated, the weight of iodoform was multiplied by .27 for the weight of acetone.

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[*] Berichte deutsch. chem. Gesellsch., 1873, 1310.

[†] Ibid., 1880, 1000.

[‡] Ann. Chem. Pharm., Suppl. VII., ccxviii. 377.

[§] In several instances the fraction was boiled with silver oxide before testing for acetone; but this seemed to have no appreciable effect on the quantity of acetone indicated by the iodoform reaction.

Fraction treated.	Specific Gravity.	Weight of Iodoform.	Weight of Acetone.	Percentage of Acetone.
54° - 56° (*a*)	0.935	0.0359	0.0097	1.04
Below 54° (*b*)	0.930	0.0648	0.0175	1.88
54° - 56° (*b*)	0.935	0.0638	0.0182	1.95
Methyl Alcohol from 54° - 56° (*b*)	0.805	0.0914	0.0247	3.07
56° - 60° (*b*)	0.830	0.0802	0.0217	2.66
65° - 68° (*c*)	0.820	0.1037	0.0280	3.41

Although the quantity of acetone in the product under consideration is sufficiently large to render further purification necessary, it is evidently much smaller than is usually observed in commercial wood spirit.

Allyl Alcohol.

The occurrence of allyl alcohol as a product of the distillation of wood was first mentioned by Aronheim,* and soon afterward Krämer and Grodzky† stated that small quantities of it may always be found in the higher fractions. In examining the aqueous part of the residue in (*c*) for this substance, after removing the water, a small amount of an oil was left, with a boiling point somewhat higher than that of allyl alcohol. It absorbed bromine readily, with the formation of a product which boiled much too low for dibromallyl alcohol, and oxidation with nitric acid gave only oxalic acid. Since from the results of Krämer and Grodzky it is usually present in wood spirit, in quantity not exceeding two tenths of one per cent, it is evidently possible that the small amount contained in 2,000 grms. might escape observation.

High Boiling Oils.

Although the composition of the higher boiling fractions was not determined with sufficiently desirable accuracy, a brief description of my attempts to isolate substances which have already been found in the less volatile portions of wood spirit may have some interest. It has already been mentioned, that beside water these fractions consisted of an oil heavier and an oil lighter than water. The heavier oil was composed chiefly of furfurol, though, as well as the water and lighter oil, it contained pyroxanthine in small quantity, which could be precipitated by the addition of sodic hydrate. 2,000 grms. of (*c*) gave 45 grms. of the lighter oil, which was pale yellow when freshly distilled, but it turned dark brown on standing. In attempting to fraction it, a constant boiling point could not be obtained between 75° and 200°. About two grms. of a substance distilled between 75° and 85°, which formed crystals with acid sodic sulphite, indicating the presence of methylethylketone; but the quantity obtained was insufficient for analysis. The penetrating odor observed in the distillate between 95° and 105° was characteristic of the allyl compounds. It was possibly due to a trace of allyl acetate, since after heating with sodic hydrate and neutralizing the solution a qualitative test for acetic acid was obtained with ferric chloride. This oil distilled for the most part between 150° and 200°. Finding, however, that a constant boiling-point could not be obtained with the supply of substance at my command, I did not consider it worth while to fraction the amount of material necessary to obtain the oil in large quantity.

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* Berichte deutsch. chem. Gesellsch., 1874, 1381.

† Ibid., 1874, 1492.

The important characters of this product, as they have appeared in the course of the preceding examination, may be summarized as follows: —

1. The high percentage of aldehyde in (*a*), of methyl acetate in (*a*) and (*b*), and of methyl alcohol in (*c*).
2. Presence of methyl formiate.
3. Absence of dimethylacetal.
4. Small percentage of acetone.
5. General purity of the product.